Development of microbial mats on contaminated soils from the former site of Vanda Station, Antarctica

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Abstract

A series of experiments were undertaken to determine the extent to which contaminants present at the site of New Zealand's now dismantled Vanda Station, Antarctica, affect the microbial communities likely to develop on such soils. Contaminated soils had higher concentrations of nutrients (N and P), organic material and some metals (Ag, Cu, Cd, Pb) relative to a control site. We found that contaminated soils supported an enhanced rate of growth and final yield of algae compared to control soils. Species composition was switched from primarily cyanobacteria to include a high proportion of green algae. A similar enhancement could be achieved by enriching control soils with N and P. Low level contamination with metals, either in soil from contaminated sites or in enrichments applied to control soils, had no deleterious effect on mat growth or composition. High levels of contamination with metals led to inhibition of growth of both algae and cyanobacteria. The algal mat growths which developed on contaminated sediments prevented nutrient contaminants within sediments from entering the water column when the mats were illuminated. However, in darkness, particularly in the absence of oxygen, nutrients were released from contaminated sediments. The freeze-thaw process also released nutrients from microbial communities. Overall, microbial mat-forming communities, which are characteristic of Antarctic inland moist habitats, were shown to be sensitive to the types of contamination which were found at Vanda Station. While the growth of mats on contaminated soils could to some extent ameliorate the effects of contaminants by restricting sediment-water exchange, this effect only occurred during periods favourable to growth and considerable release is likely during periods of anoxia, or in response to freeze-thaw processes.

Keywords: Antarctica - microbial mats - contamination - Lake Vanda

Introduction

Human activity in Antarctica inevitably leads to contamination of the environment. Current operating protocols (e.g. Vincent 1996) attempt to minimise this, but historical contamination persists in many locations, particularly those close to bases. Understanding the fates of these contaminants, and their impacts on native flora and fauna while they persist in the environment, are crucial to evaluating the extent and types of mitigation efforts which should be implemented to deal with actual and potential contamination.

From 1968 to 1993, New Zealand operated a research and recreational facility on the shores of Lake Vanda, in the Wright Valley, southern Victoria Land. During the early years of occupation, many waste streams from this station were disposed of locally. In particular, domestic liquid wastes (includes washing water, food wastes, photographic wastes and many other unspecified substances) were tipped into a small valley close to the station, which came to be known as Greywater Gully. Other areas have been contaminated with exhaust emissions and hydrocarbon spills (Sheppard *et al.* 1993). Since 1980, Lake Vanda has been rising in level (Chinn 1993), and recently concern has surrounded the possibility that leachates from Greywater Gully may be contaminating the near-pristine waters of Lake Vanda. Ultimately the lake may flood these soils, with further risk of contamination.

The consequences of contamination to the Lake Vanda ecosystem will depend on how the flora and fauna of the lake interact with specific contaminants. The community likely to show most immediate and specific response to contaminants is the microbial mat community that dominates the littoral flora of Antarctic lakes (Wharton *et al.* 1983, Vincent *et al* 1993). Not only is this community at the margins of the lake, the area most likely to come into contact with contaminants, but, because of its benthic habit, it is intimately associated with potentially contaminated sediment. A major aim of this paper was therefore to determine the effects of contaminants on development of algal mats.

Once developed, benthic microbial mats frequently form a continuous membrane covering the bottom of aquatic habitats in both Arctic and Antarctic environments (Hawes *et al.* 1993, Vezina & Vincent 1997). Such microfloral mats are known to play a role in mediating the transfer of solutes between sediments and overlying water, both by selective uptake of nutrient species, and by creating steep gradients of dissolved oxygen and nutrient ions, resulting in strongly reducing conditions in sediments (Hawes *et al.* 1993, Ellis-Evans & Bayliss, 1994). Anoxia has traditionally been associated with release of Fe-bound DRP, though recent evidence suggests that, where active microbial layers are present, this direct link may not necessarily act (Gächter & Meyer 1993). While anoxia may facilitate redox related dissolution of some ions, promotion of sulphide production through sulphate reduction in anoxic media can lead to precipitation of insoluble metal sulphides (Emerson *et al.* 1984). We therefore hypothesised that growth of microbial mats on contaminated sediments could either ameliorate or exacerbate contaminant mobility, either by uptake and sequestering of ions such as nutrients, or by creating conditions where the solubility of ions such as some metals, can be increased or decreased.

This paper reports on preliminary investigations into firstly the effects of contaminants in Antarctic soils on the development of microbial mats, and secondly into aspects of the role of these mats in mediating solute exchange between sediments and overlying waters. It draws on observations made in Antarctic lakes and ponds, and on experimental systems developed using field-collected material, under controlled laboratory conditions. Since summer and winter conditions in polar habitats are very different (e.g. Hawes *et al.* 1999) we also tested the effect of two common winter stresses on the transfer of contaminants across microbial mats. These were freezing, which has been shown to lead to nutrient release (Howard-Williams *et al.* 1997), and anoxia following ice formation and the onset of darkness (Schmidt *et al.* 1991, Kvitek *et al.* 1998).

Study Site

Lake Vanda is a large (7 km^2, 75 m deep), endorheic (closed basin) lake in the Wright Valley of southern Victoria Land (Fig. 1). Its major tributary is the Onyx River, flowing approximately 30 km westwards from its source amongst the coastal piedmont glaciers. The catchment of the lake is barren and loading of inorganic nutrients is extraordinarily low (Howard-Williams *et al.* 1997). This lake is permanently ice covered except for a narrow, intermittent and discontinuous strip around the lake edge which is ice-free for several weeks in warm summers. Having no outflow, the level of the lake is determined by the balance between inflow and loss by evaporation and ablation. In recent years, water balance has been positive, and the lake level

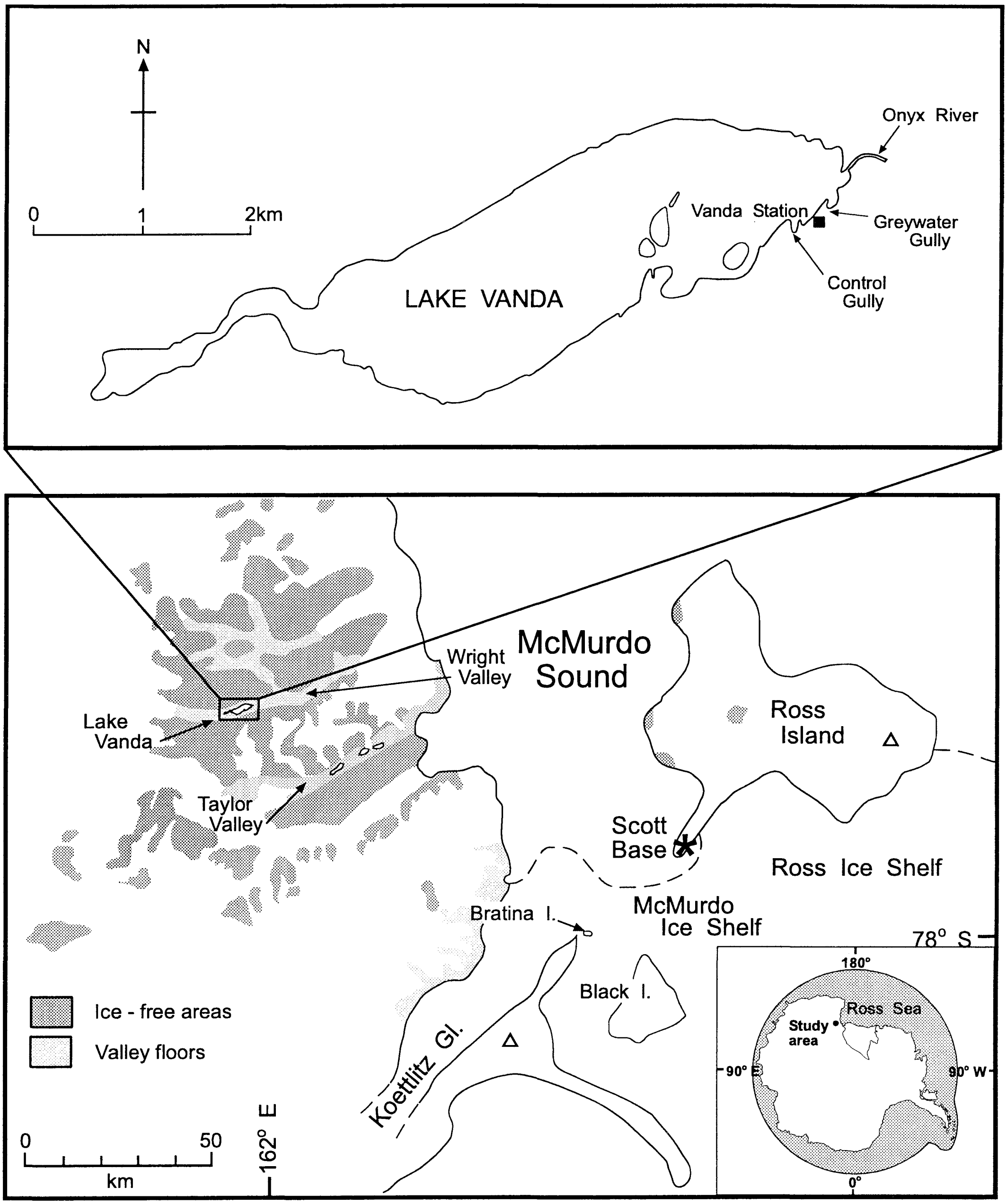

Figure 1 Map of the study area.

has risen (Chinn 1993).

New Zealand's Vanda Station was established close to the shore of Lake Vanda in 1968 (Fig. 1). It was operated for approximately three months every summer from that date until 1992, and on four occasions was occupied year round. During summer it typically housed 4-8 people. Permanent summer occupation ceased in 1992/93, and the base buildings were removed between 1993 and 1996, along with a large volume of rubbish, and heavily contaminated soils (Waterhouse 1997).

For use in laboratory microcosms replicated soil samples were collected from Greywater Gully, a known site of contamination on the shore of Lake Vanda (see Introduction). Uncontaminated soils were collected from a control site (Control Gully) of similar aspect, slope, proximity to the lake and soil type, approximately 1 km from the station site (Fig. 1). Newly developing microbial mats were collected from the margin of the lake close to the station site and used as slurries to generate inocula of natural communities for experimental studies. Mats in the Vanda margin, which had only recently been flooded, tended to be thin, and poorly cohesive. When mature such mats are up to 10 mm thick, highly cohesive and vertically laminated (Vincent *et al.* 1993). When experiments required the use of such mature mats, these were obtained from the ponds of the McMurdo Ice Shelf.

The McMurdo Ice Shelf is a region of the Ross Ice Shelf, covering 1500 km^2, where a large number of ponds occur in hollows on the surface of the moraine covered ice sheet. Howard-Williams *et al.* (1989) has described the ponds, which vary in size from a few to 30,000 m^2, in detail. A mat of cyanobacteria lines most, comprised mainly of species of *Phormidium, Oscillatoria, Nodularia* and *Lyngbya* and diatoms (Howard-Williams *et al.* 1989), which form the dominant autotrophic component of the pond ecosystems (Hawes *et al.* 1993). The ponds are ice-covered for most of the year, but melt out to varying degrees each summer according to size, conductivity and depth. The ponds have a range of conductivity, from that of freshwater to greater than that of seawater (Howard-Williams *et al.* 1989, de Mora *et al.* 1996).

Methods

Contaminated sites

Samples of contaminated and control soils were collected from Greywater and Control Gullies and returned frozen to New Zealand. The soils were characterised by measuring lake-water leachable nutrients, organic content, and the content of selected metal species. Leaching of nutrients from soils involved vigorous shaking of a known weight of soil, approximately 10 g, in 100 ml of filtered Lake Vanda water. The soil was allowed to settle, then the supernatant water was filtered (Whatman GF/F) and analysed for dissolved reactive P (DRP), NH_4-N, NO_3-N (including NO_2-N), dissolved organic N (DON) and dissolved organic P (DOP). The increase in concentration over that of lake water was taken as leachable nutrients, and calculated per unit weight of soil. All analyses were as described in Downes (1978). Organic content of dried soil samples was estimated as weight loss on ignition (500°C). Metal content of the soils was determined after acid extraction, by Inductively Coupled Plasma - Mass Spectroscopy (ICPMS). Acid extraction was by microwave digestion in nitric acid. Triplicate samples of each soil were processed.

Metal and nutrient concentrations in water in the shallows of Lake Vanda adjacent to the two soil collection sites were determined. Fifteen millilitre samples of water were preserved with Aristar nitric acid for metal analysis (ICPMS) while 100 ml samples of lake water were filtered (GF/F) and frozen for nutrient analysis. In addition, nine cores of microbial mat were taken from the shallow lake bottom adjacent to each of the soil sampling sites, three each for extraction and analysis of metals, chlorophyll-*a* and organic N and P. Analytical techniques for metals were identical to those described above for soil samples. Total N and P were determined as DRP and NH_4-N after digestion in acid persulphate, and chlorophyll-*a* spectrophotometrically after extraction in boiling ethanol.

Effects of contaminants on mat growth

The rate of development of benthic algae on the soils from Greywater Gully and the control site were determined, together with their species composition. Approximately 100 g of soil was placed in a clean, sterile 300 ml container. This was filled with sterile artificial lake water (water formulated to mimic the ionic content of Lake Vanda water using data from Webster, 1994) to within 2 cm of the surface, and 1 ml of a slurry of microbial mat from the margins of Lake Vanda added as an inoculum. Containers were incubated at 4°C, under continuous, moderate irradiance (c. 250 µmol photons m^{-2} s^{-1}), with aeration. The effects on algal growth of a number of amendments to Control Gully soil were also determined. No amendments to Greywater Gully soil were used. Amendments were designed on the basis of concentrations of contaminants known to be present at Vanda Station (Sheppard *et al.* 1993), and included nitrogen, phosphorus and metals in a range of concentrations and combinations (Table 1). Amendments were applied to soils in the experimental containers. These contaminated soils were allowed to dry, to mimic natural conditions as closely as possible, and thoroughly mixed prior to addition of artificial lake water. Each treatment was replicated four times.

The chambers were sampled after one and three months of incubation. During incubations, water levels were maintained by the addition of sterile distilled water. At each sampling, three cores (0.5 cm^2) were taken from each chamber and analysed for chlorophyll-*a*. In addition, a sample was taken from each for determination of dominant species by direct microscopic analysis.

Effects of contaminants and mat development on sediment oxygenation

During the incubations described above, it became clear that contaminated sediments from Greywater Gully quickly became anoxic after addition of water, even with 24 h light and access to atmospheric oxygen. We therefore set up an experiment to quantify this, and to determine whether development of mat communities could modify the rate and extent of anoxia. Three mesocosms were established, each comprising a 30 cm diameter cylindrical tub, 35 cm tall. Each mesocosm contained four pots, each containing approximately 100 g of either Control or Greywater Gully soil. The inner pots were embedded in a layer of acid-washed sand, which reached to the level of soil inside the pots, thus protecting the experimental soils from lateral light. Covers on the mesocosms allowed free passage of ambient air to flow into the chamber. Three treatments, designed to vary the extent of colonisation, were applied to each of contaminated and clean soil, each replicated four times. Treatments involved i) no inoculation, ii) inoculation with a slurry of microorganisms obtained from a Lake Vanda mat community, and iii) introduction of a disk of intact, cohesive mat obtained from a Bratina Island pond. In the last treatment, the disk of mat was cut to tightly fit the internal pot.

These mesocosms were incubated at 4°C, and

Table 1 Amendments to Control soils used in algal growth experiment. Control Gully and Greywater Gully soils were also incubated. 1 unit of Metals contained 0.3 µg Ag, 1.6 µg Ni, 8 µg Zn, 1.6 µg Pb, 13 µg Cu, 0.4 µg Cd.

	Nominal concentration	Control	Low P	High P	Low N
Low P	0.5 mg 100 g-1	X			
High P	5 mg 100 g-1	X			
Low N	5 mg 100 g-1	X	X		
High N	50 mg 100 g-1	X		X	
Low metals	1 unit100 g-1	X	X		X
High metals	10 units100 g-1	X	X		X

continuous irradiance (250 µmol photons m^{-2} s^{-1}), in a controlled temperature room. At fortnightly intervals thereafter, profiles of dissolved oxygen from the water overlying the mat down through the upper 2 cm of sediment were taken using a Diamond Electrotech needle oxygen electrode (tip diameter 0.1 mm), connected to a Keithly picoammeter and recording on a chart recorder. The electrode was controlled with a mechanical manipulator, which permitted 0.5 mm depth resolution, and readings were taken at 5 mm above the surface, and at 0, 1, 2, 5, 7.5, 10 and 20 mm depth into the mat/ sediment.

After a period of 60 days from each of the mesocosms, cores of mat/sediment were taken using a cut-off 60 ml syringe as a corer. These cores were divided into a series of layers, the first of which comprised any mat that had developed, and below this, slices 0.5 - 1.0 cm thick. These were analysed for organic content, acid-soluble metals and lake-water leachable nutrients, as described above.

Effects of freezing and anoxia on release of contaminants

While microbial mats may sequester contaminants during periods favourable to growth, during times of environmental stress these may be released. Two likely forms of stress for benthic communities in Antarctica are freezing (e.g. Hawes 1990, Howard-Williams *et al.* 1997), and anoxia during winter darkness (Schmidt *et al.* 1991). At the termination of the growth rate experiments (above), we subjected the mats which had developed in the culture pots to either freeze-thaw or hypoxic stress and determined the effects of these treatments on release of contaminants to the overlying water.

Freezing was accomplished by placing mats into cleaned styrene tubes containing artificial lake water and positioned in an insulated box, which was placed inside a -20°C freezer, in the dark. The box was designed to slow the rate of freezing, which was monitored using an Onsett Instruments Hobo temperature logger inside the box. After freezing, mats were thawed at 4°C and samples of water taken for analysis of nutrients, dissolved organic carbon (DOC) and metals. The yield of each of these was calculated as mg $cycle^{-1}$. After samples had been taken, the mats were subjected to a second freeze-thaw cycle. Controls comprised duplicate samples from each pot which were maintained at 4°C, in the dark.

Hypoxia was established in culture pots by placing the entire pot into dark conditions, under an atmosphere of oxygen-free nitrogen. Pots were examined after 30 days and at the end of the experiment (75 days). Where there was no smell of sulphide, dissolved oxygen concentrations were measured using a YSI oxygen electrode. When sulphide was smelt, the oxygen electrode was not used to avoid sulphide damage, and the oxygen concentrations was assumed to be zero. Liquid samples were taken for analysis of DOC, nutrients and metals. Controls were duplicate pots, which were maintained under normal growth conditions. DOC was analysed after acidification to remove inorganic carbon, using a Shimadzu TOC5000A analyser. Metals were analysed in acidified samples by atomic absorption spectrometry using an air-acetylene flame, and nutrients according to protocols described above.

Selective diffusivity of microbial mats

The final series of experiments were undertaken to determine whether microbial mats acted as selectively permeable membranes separating sediments and overlying water.

Diffusivity of ions through microbial mats was determined using a split-chamber approach. Culture medium was pumped through two chambers, using a multi-channel peristaltic pump. The upper and lower chambers (120 and 10 ml volume and 3 and 10 ml min^{-1} flow rate respectively) were separated by a sheet of microbial mat resting on a coarse nylon mesh, and solutes were free to diffuse through the mat from one chamber to the other. The upper chamber was continuously aerated to maintain vigorous mixing, while the lower relied on the rapid through-flow of medium to ensure mixing. The mat was horizontally oriented, and could be illuminated from above; the whole apparatus being maintained at 10°C in a controlled temperature room. Culture medium was designed to mimic the major ion composition of pond water from which the mats were obtained (from data in Whitehead, 1989). Medium flowing through the lower chamber was enriched with nutrients (DRP and NH_4-N), together with bromide, which we considered would act as a conservative tracer. The equilibrium concentrations of the various enrichments established in the upper chamber as a result of diffusion through the mat were determined by sampling the upper chamber until concentration stabilised. The rate of transfer of enrichment to the upper chamber was calculated as

$$R = (C_U \times F_U)/A$$

Where R is diffusion rate (μmol cm^{-2} s^{-1}), C_U is concentration in upper chamber (μmol cm^{-3}), F_U is flow rate through upper chamber (0.075 cm^{-3} s^{-1}) and A is mat area (cm^2). The thickness of the mat was measured (h, cm), the concentration gradient under equilibrium conditions calculated ($\Delta C = (C_u - C_L)/h$; μmol cm^{-4}), and the diffusivity of the mat (D; s cm^{-2}) calculated according to Fick's Laws of diffusion as

$$D = R/\Delta C$$

Results

Characterisation of Greywater Gully and Control Gully soils

Greywater Gully contained much higher levels of inorganic and organic nutrients than the control site (Table 2). Nitrogen compounds were predominantly as oxidised inorganic forms at the control site, whereas reduced and organic N were more common than NO_3-N at Greywater Gully. Similar analyses of experimentally enriched control soils, to place them in the context of Greywater Gully, showed that extractable DRP increased to 12.0 ± 0.2 and 155 ± 3 μg g^{-1} for low and high enrichments, and NO_3-N to 29 ± 1 and 311 ± 8 μg g^{-1}. These values were greatly in excess of those found in Greywater Gully sediments. Greywater Gully soil showed markedly elevated concentrations of Ag. Cd and Pb, with a slightly elevated Cu level relative to the control site while Ni, Cr, and Zn were either similar to or less than the control site (Fig. 2). Analysis of water lying in Greywater Gully showed that the elevated levels of Ag, Cr and Cd in soils were reflected in overlying water (Table 3).

While there was evidence of persistent contamination of Greywater Gully, there was no evidence for these contaminants reaching Lake Vanda. Lake water and microbial mats adjacent to the site of contamination showed elevation concentrations of only Ag and Cd compared to the control site (Table 4), and show no difference in the amount of phototroph biomass as chlorophyll-*a*, nor in particulate nitrogen or phosphorus (Table 5). Microscopic analysis showed no difference in species composition of mats from the two shallow lake sites (data not

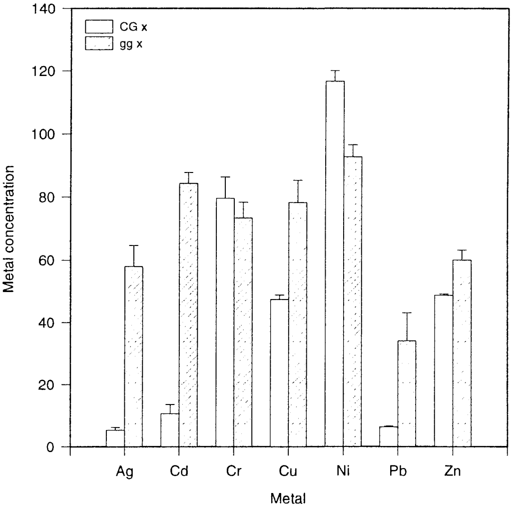

Figure 2 Content of selected metal species in soils from Greywater Gully and Control Gully. Mean ± SD, n=3. Ag, Cd, Cr, - μg kg^{-1}, Ni, Cu, Pb mg kg^{-1} × 10, Zn mg kg^{-1}.

Table 2 Lake-water extractable nutrient contents of Greywater and Control Gully soils, and % organic content (defined as weight loss on ashing). Nutrient concentrations are in $\mu g\ g^{-1}$ dry weight of soil. Values are mean ± SE, n=3.

Site	DRP	NH_4-N	NO_3-N	DOP	DON	%Organic
Greywater	0.73 ± 0.09	1.71 ± 0.12	0.18 ± 0.01	0.48 ± 0.06	8.77 ± 0.58	1.08± 0.04
Control	0.02 ± 0.00	0.13 ± 0.02	0.61 ± 0.06	0.02 ± 0.00	0.00 ± 0.00	0.34 ± 0.01

Table 3 Concentrations of total metals in Vanda water samples, January 1997. All units are mg m^{-3}, mean ± SD, n=3, analysed by ICPMS.

Metal	Greywater Gully	Vanda Bay	Control Bay
Ag	<0.5	<0.5	<0.5
Cd	0.20 ± 0.02	<0.01	<0.01
Cr	2.4 ± 0.1	0.31 ± 0.23	0.69 ± 0.06
Cu	20 ± 1	0.34 ± 0.31	0.43 ± 0.34
Ni	0.5 ± 0.4	<0.1	<0.1
Pb	0.42 ± 0.30	0.22 ± 0.12	0.11 ± 0.06
Zn	5.8 ± 1.3	6.6 ± 3.9	1.8 ± 0.9

Table 4 Concentrations of acid-soluble metals in mat samples taken from Lake Vanda shallows, adjacent to Greywater and Control Gullies, January 1997. All units are mg kg^{-1}, except those marked † which are $\mu g\ kg^{-1}$. mean ± SE, n=3, analysed by ICPMS. * indicates that Vanda Gully samples were significantly greater than Control Gully (*t* test, $P<0.05$).

Metal	Vanda Gully	Control Gully
Ag†	7.2 ± 2.6*	3.7 ± 0.6
Cd†	21 ± 2*	12 ± 2
Cr	1.2 ± 0.1	1.5 ± 0.2
Cu	6.5 ± 0.3	8.0 ± 1.1
Ni	1.7 ± 0.2	1.9 ± 0.2
Pb	1.7 ± 0.1	1.0 ± 0.1
Zn	5.8 ± 0.2	5.0 ± 0.8

Table 5 Composition of microbial mats from Vanda Gully and Control Gully in January 1997. PN and PP are particulate nitrogen and phosphorous respectively. Data are mean ± SE, n=3.

Determinant	Vanda Gully	Control Gully
PN mg g^{-1}	141 ± 27	116 ± 23
PP mg g^{-1}	140 ± 5	109 ± 1
Chlorophyll-*a* mg cm^{-2}	2.06 ± 0.92	1.84 ± 1.05

shown).

Effects of contaminants on mat growth

The yield of algal biomass at the end of the experiment (three months incubation), measured as chlorophyll-*a*, was much higher on soils from Greywater Gully than from the control site (Fig. 3). Clearly the stimulatory effects of enrichment of the soil overcame any inhibitory effect of potential toxins. The only experimentally contaminated soils which approached the yield of Greywater Gully were those enriched with large amounts of both N and P. Of the single additions, P gave the highest yield, though none of these were significantly higher than the control after three months of growth. Addition of a single unit of metal contaminants had no impact on chlorophyll-*a* yield, whereas increasing this to 10 units led to almost no algal growth. Yield after both one and three months incubation was significantly increased by addition of N and P (Fig. 3). In contrast, after one month, Greywater Gully soils had similar chlorophyll-*a* amounts to control soils and a significant yield increase was only seen after three months. This suggests that growth rates in the first month were no higher in Greywater Gully soils than Control soils, but that the higher levels of nutrients may have permitted growth to continue for longer.

Part of the reason for differences in growth rates and yields may be that different dominant taxa were favoured by different treatments (Table 6). Filamentous cyanobacteria were the dominant organisms in microbial mats growing at the edge of Lake Vanda and hence in the inoculum used in these experiments, and were present in all treatments. Addition of nutrients, particularly both N and P, increased the abundance of chlorophytes more than cyanobacteria. This is consistent with field observations, where, over summer, we saw a bloom of *Stichococcus* sp. in a stream draining a small pond in Greywater Gully.

Effects of contaminants and mat development on sediment oxygenation

The development of oxygen profiles in the two types of soil on flooding with water was consistent with the effects of organic contamination of Greywater Gully (Fig. 4). When Greywater Gully soils were flooded, oxygen was depleted to zero within 5 mm of the surface within seven days (time series data not shown) and this persisted to at least one month (Fig. 4, B, D, F). While oxygen was depleted in flooded Control Gully soils, anoxia was only reached at 20 mm depth after one month (Fig. 4, A, C, E), while shallower depths remained oxic. When mat development was enhanced by the addition of an inoculum of Vanda mat species, this made little difference to the ultimate oxygen profile in the soils compared to no inoculum (Fig. 4 C, D). The addition of a complete mat initially made little difference to Greywater Gully soils in terms of rate of oxygen depletion or profile shape. However, after one month, the mat was sustaining a very steep oxycline close to the underside of the mat by reducing the oxygen concentration at 2 mm depth relative to the other treatments (Fig. 4 C, D). However, on the control soils a complete mat on the soil surface promoted oxygen depletion within the upper part of the soil profile, either through reduced permeability or by increasing oxygen demand.

Sectioning of sediments underlying mats at the termination of this experiment after sixty days showed no consistent patterns of distribution of metals (data not shown). There was no significant difference between any of the mat treatments on the distributions of metals within cores, and no significant difference in the metal contents of the microbial mats growing on the two types of sediment, though Ag, Cu and Pb were slightly higher on Greywater Gully soil. Anoxic or oxic conditions within sediments seemed to make no difference to metal mobilisation within sediment since there was no apparent increment of metals through the profiles.

Effects of freezing and anoxia on release of contaminants

In darkness, under a low-oxygen atmosphere, the oxycline in Greywater Gully samples quickly moved up through the mat to reach the overlying water. Within 30 days all Greywater Gully samples smelt strongly of sulphide. Anoxia took considerably longer to establish in Control Gully samples. Most Control Gully treatments had oxygen concentrations of 3-5 mg l^{-1} after 30 days, falling to <2 mg l^{-1} after 75 days. Exceptions were the +50NP treatment, which had produced the highest biomass, and where sulphide was detectable after 30 days, and the +5NP treatment where it was detected at 75 days. Samples treated with +10 units of Heavy metals, i.e. with virtually no mat development, remained at 7 mg l^{-1} dissolved oxygen after 30 days, and fell to 4 mg l^{-1} after 75 days.

Under conditions where the oxycline had entered the water column, we expected the characteristics of sediment/water exchange for both nutrients and redox-related metals to change. Indeed this was partly the case for those treatments containing higher biomass such as Grey control and Clean 50 N/P. In these sites an initial pulse of DOC, NH_4-N, and DRP was released into the water (Table 7). This was reversed after 75 days for both DOC and DRP with apparent consumption occurring. NH_4-N continued to be released in the treatments from Greywater Gully and Control Gully. Control Gully soils amended with 10 units of metals, enough to inhibit mat growth, showed release of NH_4-N during anoxia, though at levels lower than those without heavy metals, or from Greywater Gully.

In unamended Control Gully soils, neither DRP, nor NO_3-N was found to accumulate in the overlying water during hypoxia, though some

Table 6 Taxa encountered in mats developing on a range of amended soils. +++ indicates abundant, ++, common and + occasional. CC= Control Gully, GG = Greywater Gully

Species	CC, control	CC, 1hm	CC, 10 hm	CC, 5P	CC, 5N	CC, 5N5P	CC, 50N, 50P	GG, Control
Cyanophyta								
Oscillatoria, 2 µm wide	+++	+++	+	++	+++	+++		+++
Oscillatoria, 4 µm wide							+++	
Oscillatoria, 10µm wide			+	++		+		
Oscillatoria, 12.5 µm wide								
Lyngbya, 1.5 µm			+					
Phormidium frigidum			+					
Nodularia sp.								+
Anabaena sp.								++
Bacillariophyta								
Pinnularia sp.					+	+		
Hantzschia amphioxys				++		+	+	
Navicula muticopsis	+				+		+	
Navicula cryptocephala	+				+	+	+	
Navicula paludosa	+	+			+			
Stichococcus sp	+	+			+	++	++	++
Chlorophyta								
Green flagellates		+						+
Green Granular Spheres	+	+		+		++	+++	+
Binuclearia sp.								++

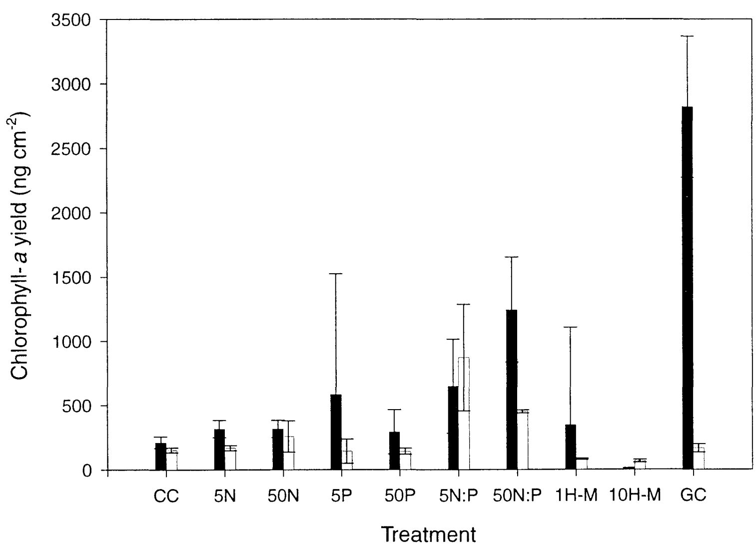

Figure 3 Yield of algal biomass, as Chlorophyll-*a* on soils from Greywater Gully, and from Control Gully with and without amendments. Median, 25 and 75% quartiles, n=5. The left bar is the final yield (after three months), the right bar the yield after one month.

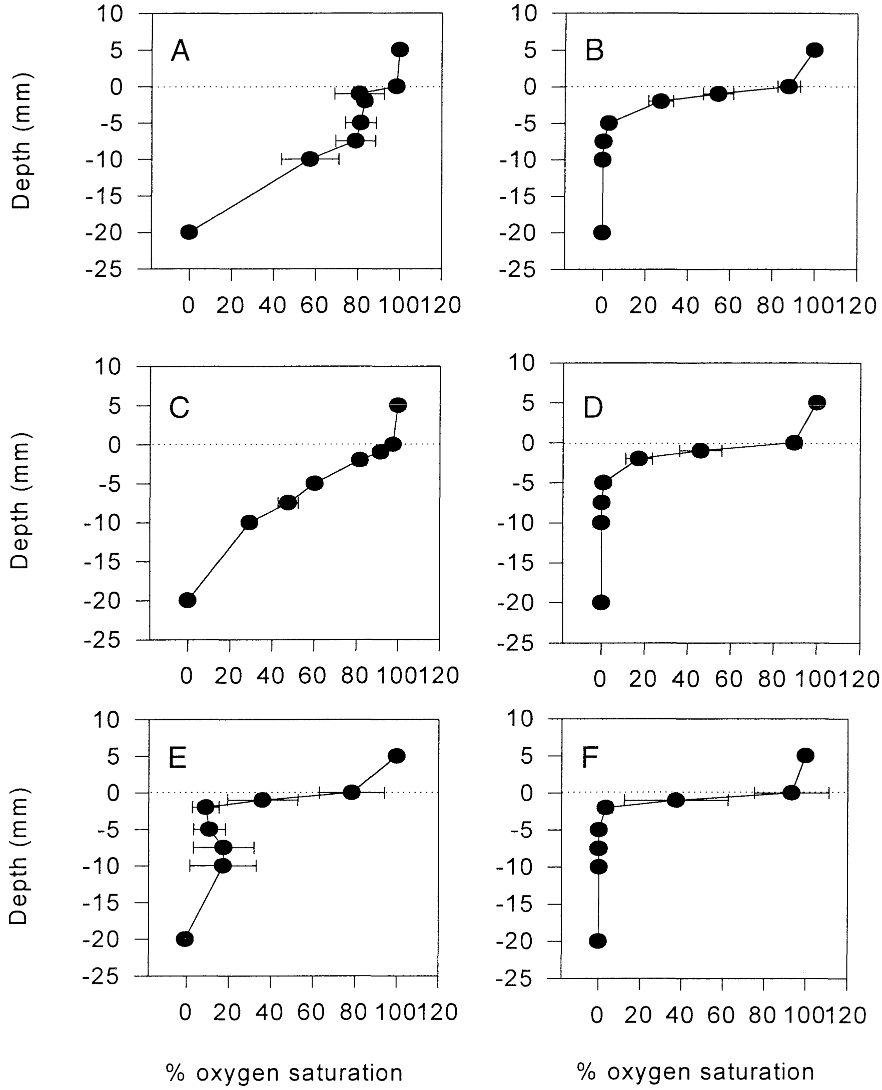

Figure 4 Oxygen concentration profiles through Greywater Gully (A, C, E) and Control Gully (B, D, F) soils after flooding with water, with three colonisation regimes; A, B, no inoculum, C, D, inoculated with slurried Vanda microbial mat, E, F, inoculated with fully developed mat from Bratina Island pond. All treatments were incubated for 60 days.

NH_4-N was released. In Greywater Gully soils, a measurable amount of DRP was released into the water during anoxia, while a similar amount of NH_4-N as above soils from Control Gully accumulated (Fig. 5). Control Gully soils amended with 10 units of metals, enough to inhibit mat growth, still showed release of NH_4-N during anoxia. When soils were amended with both DRP and metals, i.e. mat growth was inhibited, release of DRP was much more than in the DRP-only enrichments (Fig. 5). Conversely, enrichment with metals and N did not further stimulate anoxic N release. Heavy metal and 50N treatments of control soils were the only ones to release measurable amounts of NO_3-N.

As no mat developed on the soils amended

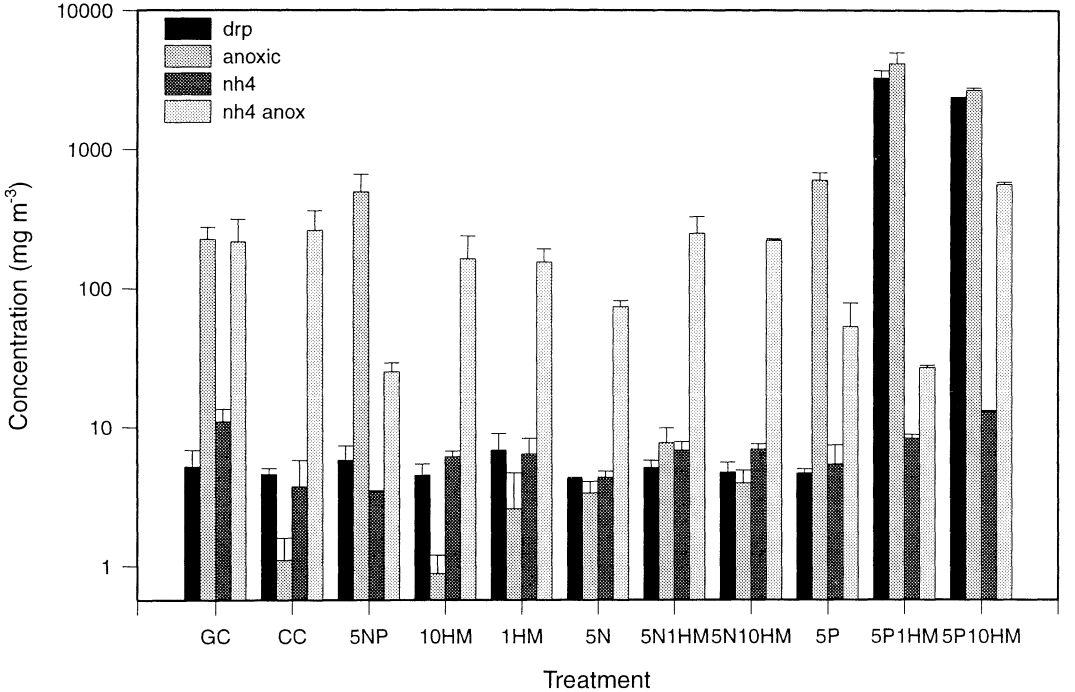

Figure 5 Concentration of nutrients in water overlying experimental communities developed on Greywater Gully and Control Gully soils, when subject to anoxic or oxic conditions. Bars are mean ± two SEM.

Table 7 Average values of release of DOC and nutrients for the three treatments Clean control (Control Gully no enrichments), Clean 50 N/P (Control Gully plus DRP and NO_3-N), and Grey control (Greywater Gully no enrichments). All values are in mg cm^2. In freeze-thaw treatments T=1 and T=2 are freeze-thaw cycles, while in the anoxic treatments, they are 30 and 75 days after anoxia. Negative values imply uptake of determinant.

		Clean control		Clean 50 N/P		Grey control	
		T=1	T=2	T=1	T=2	T=1	T=2
DOC	Anoxic	1.47	9.33	412.92	-217.83	403.46	-92.15
	Freeze/Thaw	0.7	0.0	2.00	6.61	14.9	15.4
DON	Anoxic	-0.97	0.26	0.82	-5.98	-1.50	3.61
	Freeze/Thaw	0.0	0.0	0.45	0.69	<0.01	0.99
NO_3-N	Anoxic	0.06	5.59	-0.18	0.19	0.02	0.19
	Freeze/Thaw	0.31	0.35	0.29	0.24	0.31	0.23
NH_4-N	Anoxic	1.38	-0.94	0.81	40.70	0.99	9.38
	Freeze/Thaw	0.0	0.0	0.04	0.07	0.01	0.03
PO_4	Anoxic	0.0	0.0	36.65	-30.95	1.07	0.17
	Freeze/Thaw	0.03	0.0	0.0	0.0	0.0	0.0

with 10 units of metals these treatments were not included in the Freeze / Thaw experiments. Freezing induced some loss of DOC in all treatments in the range of 2 to 8 µg cm^2, except those soils from Greywater Gully, approximately 15 µg cm^2. A similar trend occurred with DON, with values approximately 10 fold lower than DOC (Table 7). Freezing did not induce loss of any measurable quantities of DRP, and only small quantities of NH_4-N after each F/T cycle. However NO_3-N was lost from all mats upon freezing at a surprisingly consistent rate of 0.3 µg cm^2 per cycle in all treatments.

Selective Diffusivity of microbial mats

Diffusivity of mats to Br, under an experimental regime which imposed a gradient of 3-5 (µmol cm^{-3}) cm^{-1}, was consistent under both light and dark conditions, at $5.2 \pm 0.7 \times 10^{-7}$ $cm^2\ s^{-1}$ (mean ± SD, n=6). Diffusivity of DRP was undetectable under illuminated conditions ($<4 \times 10^{-8}$ $cm^{-2}\ s^{-1}$), despite a DRP gradient of >1 (µmol cm^{-3}) cm^{-1} across the mat. In the dark, diffusivity was similar to that of Br, at $3.1 \pm 0.9 \times 10^{-7}$ $cm^2\ s^{-1}$. NH_4-N also showed a distinct increase in diffusivity from light to dark, with a value of $1.1 \pm 0.8 \times 10^{-6}$ $cm^2 s^{-1}$ in the dark, compared to a value below detection limits ($<8 \times 10^{-8}$ $cm^{-2}\ s^{-1}$) in the light.

Discussion

This study has shown that the contamination of the soil of Greywater Gully, during nearly 30 years of occupation, has created conditions which will affect the development of sediment chemistry and biological communities should these soils become submerged.

Organic contaminants have increased the sediment oxygen demand, resulting in highly reduced conditions developing quickly within a few mm of the surface when inundated. Since similar conditions occur under well developed mats where no contamination has occurred, this is unlikely to adversely affect community development in the long term. Cyanobacteria are particularly tolerant of conditions that would be adverse to other groups. *Phormidium* spp. are able to withstand anoxia, with high concentrations of sulphide and some species are even able to utilise sulphide in anoxygenic photosynthesis (Stal 1995). They are also commonly used in wastewater treatment, where their ability to tolerate high concentrations of DOC and many metals is advantageous.

Contamination by metals may affect the chemical composition of the algal material produced, but the observed level of contamination is unlikely to affect community composition or rate of development. Contaminated soils contained up to an order of magnitude more metals than control soils, yet even these levels were many orders of magnitude less than genuinely contaminated temperate sediment. Cd levels of 0.008 µg g^{-1} in contaminated Vanda soils compares to 10 µg g^{-1} in lower Rhine sediments, and Pb levels of 3 µg g^{-1} to over 100 µg g^{-1} (ten Hulscher *et al.* 1992). Growth was inhibited only when sediments were enriched with metals at the high level, when Rhine concentrations might have been approached. It is therefore not surprising that the small amount of contamination seen in the soils of Greywater Gully was insufficient to inhibit growth.

The absence of significant release of metals from the experimental systems, even under prolonged darkness and hypoxia, was indicated by the failure of metal concentrations in sediments to decrease over time, or for measurable metal concentrations to accumulate in anoxic conditions. This may be due to several reasons, but tends to suggest that metals were tightly bound to mineral particles. The lack of any interaction with the microfloral mat is indicated in that metals were not released even from sediments enriched to levels that prevented a mat developing. In the Greywater Gully soils, the strong smell of sulphide in overlying water is indicative of extensive sulphate reduction in the sediments. Precipitation of metal sulphides under such conditions may prevent metal ion migration into the water column (Emerson *et al.* 1984, Wallman 1992). Iron sulphides produced in this manner, along with other metal contained within sulphide complexes, are often ultimately transformed into pyrite, resulting in long-term sequestration (Krumbein & Swart 1983).

The most conspicuous effect of sediment contaminations would seem to be exacted by nutrient enrichment. Nutrient enrichment affected both the type of phototrophic community which will initially develop, and the rate of development. It is not surprising that Antarctic mat communities respond similarly to temperate ones by increasing growth rate when nutrient enrichment occurs. Proliferations of green algae are common in nutrient enriched benthic communities, even in other Antarctic environments (Hawes 1989).

There was some evidence that microbial mats acted as semipermeable membranes to sediment solutes, though, where these solutes were biologically active, this was restricted to periods when conditions were favourable to growth. The observation that release and diffusivity of mats to nutrients differed between light and dark treatments are consistent with previous findings. Kelderman *et al.* (1988) reported that, in sediments covered with a microfloral mat, rates of release of both NH_4-N and DRP were 85% lower in the light than in the dark. They attributed this to a combination of redox-related effects and light-dependent uptake by the photosynthesising microfloral layer.

In conclusion, the types of contamination of soils that have occurred during 20 years of occupation at Vanda Station include those that can affect the growth of indigenous algae and cyanobacteria. Release of biologically active substances from contaminated sediments is to some extent controlled by microflora, with nutrient release almost eliminated under illuminated conditions. However, the organic content of the sediments also plays a major role in determining its geochemistry, particularly in the way it affects the redox state of the sediment. When organic content is high, anoxia develops rapidly. When initial organic content is low, sediment anoxia is likely to develop more slowly over time as a result of release of organic material from the developing microbial layer. Surprisingly, freeze-thaw cycles would have little effect on the release of materials from contaminated sediments, though periods of anoxia are likely to result in enhanced release of nutrients, though not metals.

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